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# Continental Runoff of Solid Matter as a Source of Dissolved Calcium in the Ocean

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Abstract—It was found in the experiments that the transfer of calcium from the solid phase to the dissolved state took place under the interaction of terrigenous matter (bottom sediments from the freshwater lake) with the solutions modeling the interstitial waters of the sediments of high-productive regions of the ocean. This calcium might later bind the autochthonous  $CO_2$  formed in the ocean under the oxidation of organic matter. According to the data of the three-week experiment, 1 g of the terrigenous matter evolved on average ~2.3 mg Ca<sup>2+</sup> into interstitial solutions, which conforms to the involving of exclusively surface layers of the grains of the solid phase into the reaction. In view of the true rate of halmyrolysis of the grains of terrigenous silicates (a few µm/year), at the value of the continental runoff of solid matter being equal to 16 billion t/year, the amount of dissolved calcium supplied to the ocean as a result of the transformation of the terrigenous sedimentary matter at the stage of diagenesis amounts to 250–440 million t/year and over. These values are 3- to 5-fold higher that the amount of calcium in the continental runoff of dissolved matter supplied by the erosion of silicates and capable of forming carbonate sediments in the ocean under the interaction with autochthonous CO<sub>2</sub>, unlike the calcium that is product of the dissolution of carbonate rocks.

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### **INTRODUCTION**

As evident from the consideration of the present geochemical balance of organic and inorganic carbon in the ocean, the main intrabasin process is the oxidation of organic matter and the following transfer of the formed inorganic carbon into the composition of carbonate sediments [8]. At that, a powerful source of reactive calcium and magnesium must exist in the ocean, because the amount of dissolved forms of these elements required for the transformation of the oxidation products of organic carbon into carbonate sediments is over twice as high as their supply with the continental runoff.

Formerly, the authors showed that calcium was leached from the solid phase under the interaction of fresh pyroclastic matter and seawater [6]. However, this process could not compensate for the deficiency of calcium resulting from the balance of carbon in the ocean. One may suppose that calcium is also leached from the terrigenous silicates supplied to the ocean within the continental runoff of solid matter in amounts much exceeding the supply of pyroclastic matter.

The oxidation of organic matter is most intense in the bottom sediments of high-productive regions of the ocean, where, under a high rate of sedimentation, sulfates are the primary oxidants:

$$SO_4^{2-} + 2CH_2O = H_2S + 2HCO_3^{-}.$$
 (1)

In the course of sulfate reduction (Eq. 1), the equivalent substitution of sulfates with carbonate alkalinity proceeds. At that, the interstitial waters of the sediments from high-productive regions of the ocean show the increase of the carbonate alkalinity to 20-30 mg-equiv/L and over. In most cases, this is not accompanied by the formation of solid carbonates of calcium and magnesium because of the high partial pressure of CO<sub>2</sub> causing the increase of the acidity to pH < 7.5. Theoretically, these conditions make possible the partial transfer of calcium from terrigenous silicates into the dissolved state. The present study aimed to verify this hypothesis in experiments.

#### MATERIALS AND METHODS

The sample of brown ooze collected in Pes'vo Lake (Tver oblast, Russia) was used as the terrigenous matter for the experiments. The mineral and grain-size composition of the sample are given in Tables 1 and 2. The solutions modeling the interstitial waters of the sediments of high-productive regions of the ocean coincided with standard seawater of 35‰ salinity (Table 3) excluding bicarbonates and sulfates with the contents varying according to the stoichiometry of sulfate reduction (Table 4).

The experiments were carried out in sealed polypropylene bottles of 368 mL volume, each containing 200 mL of interstitial solutions of each of mod-

Table 1. Mineral composition of the ooze from Lake Pes'vo

Mineral phase	% of the sum
Smectite	1.3
Mixed-layered mica-smectite regulated with the ratios of the packets of mica and smectite being equal to	
~65:35	1.3
~85:15	10.6
Hydromica	32.5
Caolinite	15.6
Magnesian-ferrian chlorite	6.3
Quartz	19.3
Potassic feldspar	8.7
Plagioclase	4.4

Table 2. Grain-size composition of the ooze from Lake Pes'vo

Grain size, µm	Integrated volume, %
≤0.5	0.30
≤1	1.26
≤5	8.94
≤10	15.65
≤50	59.50
≤100	84.53
≤250	96.46
≤500	99.31
≤600	99.75
≤700	99.97
≤800	100
≤900	100
≤1000	100

**Table 3.** Preparation and composition of the artificial seawater of 35% [5]

Amoun per 1 L of	t of salt f seawater	Ion	Concentration, mg-equiv/L
salt	weighed sample, g	Na <sup>+</sup>	419.32
NaCl	24.51	$K^+$	10.46
KCl	0.78	$Mg^{2+}$	54.68
$MgCl_2 \cdot 6H_2O$	11.11	Ca <sup>2+</sup>	10.63
CaCl <sub>2</sub>	1.18	Cl-	560.40
$Na_2SO_4$	4.11	$SO_{4}^{2-}$	28.94
NaHCO <sub>3</sub>	0.20	Alk*	2.38

\* Carbonate alkalinity.

$$HCO_{3}^{-} + H^{+} = CO_{2} + H_{2}O,$$
 (2)

coincided with the partial pressure of CO<sub>2</sub> ( $P_{CO_2}$ ) in 168 mL of the gaseous phase required to provide the value of the pH ~7.5. To calculate the equilibrium (2),

the amount of carbon dioxide formed in the reaction

$$K'_{\rm H}K'_{\rm I} = \frac{a_{\rm H^+}[{\rm HCO}_3^-]}{P_{\rm CO_2}},$$
 (3)

the constants of Henry  $(K'_{\rm H})$  and of the first step of dissociation of carbonic acid in seawater  $(K'_{\rm 1})$  were used, being equal to 0.0129 and  $1.0 \times 10^{-6}$ , respectively [5].

The samples were mixed continuously with a shaker for 8-10 h a day at  $22 \pm 1$  °C for three weeks and then filtered through a 0.22-µm membrane filter. The pH values and carbonate alkalinity (Alk) were determined in the filtrates and in the initial solutions using potentiometry and volumetry, respectively. The concentrations of calcium and magnesium were determined by complexometry. The content of silicon was determined by colorimetry with ammonium molybdate [4]. The error of the pH measurements was  $\pm 0.005$  units or less; those for the carbonate alkalinity and the calcium and magnesium contents (in two parallels) were within  $\pm 1\%$  and within  $\pm 3\%$  for the silicon concentrations.

#### **RESULTS AND DISCUSSION**

The results of the experiments are presented in Table 5. It is seen that the interaction between the bottom sediments from the freshwater lake and the solutions modeling the interstitial waters of the sediments of high-productive regions of the oceans causes the increase of the dissolved calcium and silicon concentrations and the growth of the solid phase—solution mass ratio within the whole range of carbonate alkalinity. At that, the dependence of varying the calcium concentrations in a solution ( $\Delta$ [Ca], mg-equiv/L) on the mass of the sediment sample (*m*, g) was the same for all the experiments (Fig. 1) and described by the linear equation

$$\Delta$$
[Ca] = 0.1144*m*, (4)

according to which 0.1144 mg-equiv, or 2.3 mg, Ca is transferred from 1g of sediment to the solution.

Because the value of the alkalinity was practically invariable in each of the series of experiments, the solutions were not supersaturated in  $CaCO_3$ , and the obtained data conform to the process of calcium leaching from terrigenous silicates with no formation of diagenetic carbonates.<sup>1</sup> In this case, the dissolved calcium diffuses into the water mass, where it takes part in the formation of carbonate sediments far beyond the bounds of the mobilization areas. However, under the saturation of the interstitial solutions in CaCO<sub>3</sub>, the calcium losses its mobility and becomes bound by autochthonous CO<sub>2</sub> in the direct reaction of silicate substitution for calcite.

Unlike calcium, the concentration of magnesium was constant in all the experiments. This points to its indifference to the process of the interaction of terrigenous silicates and interstitial solutions of the sediments of high-productive regions of the ocean. (These solutions are characterized by high values of the carbonate alkalinity).

The concentration of silicon increased nonlinearly with the growth of the solid phase—solution mass ratio (Fig. 2), which is described by the hyperbolic function

$$\Delta[\mathrm{Si}] = \frac{Km[\mathrm{Si}]_{\mathrm{eq}}}{1+Km},\tag{5}$$

where  $\Delta$ [Si] and [Si]<sub>eq</sub> are the increase of the silicon concentration resulting from the dissolution of the solid phase in the experiment and the maximum concentration of silicon in the solution ( $\mu$ M), respectively; *m* is the mass of the solid phase per unit of the solution volume, g/L; and *K* is a constant parameter. Rearranging Eq. (5) into the linear form

$$y = a + bx, \tag{6}$$

where  $y = 1/\Delta[Si]$ ; x = 1/m;  $a = 1/[Si]_{eq}$ ;  $b = 1/(K[Si]_{eq})$ , one may calculate the maximum concentration of silicon in the solution  $[Si]_{eq} = 1/a$  and the parameter K = a/b. The values of  $[Si]_{eq}$  and K for different series of the experiments (Table 6) were close to each other and amounted to  $142 \pm 11 \mu$ M and  $0.14 \pm 0.02$ , respectively. The calculated value of the maximum concentration of silicon was lower by about an order of magnitude than the seawater solubility of amorphous silica [10]. This latter, according to Ostwald's rule, must be a primary mineral phase in the products of the transformation of terrigenous silicates. This fact points to the incomplete transformation of the silicate fraction of the ooze, which does not attain the formation of free SiO<sub>2</sub> as under the erosion on land.

According to Eq. 4 generally describing the experimental data, about 2.3 mg Ca<sup>2+</sup> of 1 g of terrigenous matter pass into the solution under the interaction with interstitial waters of the sediments of high-productive regions of the ocean. In view of the total mass of the continental runoff of solid matter of ~16 billion t/year [1, 2, 9, 11], this is equivalent to the release of  $16 \times 10^{15}$  g/yr × 2.3 ×  $10^{-3}$  g Ca/yr =  $3.68 \times 10^{13}$  g Ca/year, or ~ 37 million t Ca per year. This amount is as little as

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**Table 4.** Carbonate alkalinity and concentrations of sulfate

 ions in the solutions simulating the interstitial waters of the

 sediments in high-productive regions of the ocean

Solution	<b>PW-1</b>	PW-2	PW-3	PW-4
Alk, mg-equiv/L	8.44	13.85	19.50	30.25
$SO_4^{2-}$ , mg-equiv/L	52.7	46.7	40.7	30.7

5% of the continental runoff of dissolved calcium. However, this value must be considered as obviously underrated because the moving of the front of the reaction within the solid phase is extremely slow, and only the surface layers of the grains have time to react in view of the short duration of the experiments.

Assume that the grains of ooze are spherical and the surface layers have reacted with the aquatic media to a depth of  $x \mu m$  during the experiment. Hence, the fraction of the unreacted matter for a grain of  $d (\mu m)$  diameter should be equal to

$$\alpha_{n/r} = \left(\frac{d-x}{d}\right)^3.$$
 (7)

Based upon the measured function of the distribution of the grain-size composition of the treated sample of ooze (Table 2), one may calculate the mass portions of the different grain-size fractions. Taking their average diameters, the proportions of the unreacted ( $\alpha_{n/r}$ ) and reacted matter ( $\alpha_r = 1 - \alpha_{n/r}$ ) in each of the fractions may be evaluated, and then the total volume of the reacted sediment should be obtained. According to [3], under the oxidative conditions, the rate of halmyrolysis



**Fig. 1.** Variations of calcium concentrations in modeling interstitial solution with the increase of the mass (m) of the sample of freshwater ooze. The solutions are as follows: (1) PW 1, (2) PW 2, (3) PW 3, and (4) PW 4.

<sup>&</sup>lt;sup>1</sup> The undersaturation of the interstitial solutions in CaCO<sub>3</sub> is common for the bottom sediments in oceans and seas at both low and high values of the carbonate alkalinity.

	0										0		
	pН	Alk	, mg-equ	ıiv/L	[Ca]	, mg-equ	iv/L	[Mg]	, mg-equ	ıiv/L		[Si], µM	
m <sub>solid phase</sub> , g/L	libri- um	initial	equilib- rium	ΔAlk	initial	equilib- rium	∆[Ca]	initial	equilib- rium	$\Delta[Mg]$	initial	equilib- rium	Δ[Si]
						Solution	n PW-1						
1	7.60	8.44	8.44	0.00	20.67	20.67	0.00	109.87	109.97	0.10	6.2	21.3	15.1
2	7.51	"	8.44	0.00	"	20.88	0.21	"	109.97	0.10	"	32.7	26.4
5	7.32	"	8.42	-0.02	"	21.20	0.53	"	109.86	-0.01	"	54.5	48.2
10	7.13	"	8.42	-0.02	"	21.84	1.17	"	109.84	-0.02	"	83.3	77.1
20	6.89	"	8.42	-0.02	"	23.00	2.33	"	109.93	0.06	"	128.3	122.0
I		1		1	1	Solution	n PW-2						
1	7.79	13.85	13.85	0.00	20.67	20.78	0.11	109.87	109.97	0.10	6.0	24.2	18.2
2	7.73	"	13.85	0.00	"	20.88	0.21	"	109.97	0.10	"	33.3	27.3
5	7.55	"	13.80	-0.05	"	21.09	0.42	"	109.96	0.10	"	59.0	53.0
10	7.33	"	13.85	0.00	"	21.84	1.17	"	109.84	-0.02	"	89.1	83.2
20	7.08	"	13.80	-0.05	"	23.00	2.33	"	109.93	0.06	"	135.1	129.1
						Solution	n PW-3						
1	7.63	19.50	19.45	-0.05	20.67	20.67	0.00	109.87	109.97	0.10	6.8	23.5	16.6
2	7.60	"	19.50	0.00	"	20.88	0.21	"	109.97	0.10	"	33.3	26.4
5	7.48	"	19.45	-0.05	"	21.20	0.53	"	109.86	-0.01	"	62.1	55.3
10	7.33	"	19.40	-0.10	"	21.73	1.06	"	109.95	0.08	"	92.7	85.9
20	7.14	"	19.30	-0.20	"	23.00	2.33	"	109.93	0.06	"	143.8	136.9
						Solution	n PW-4						
5	7.67	30.25	30.25	0.00	20.67	21.09	0.42	109.87	109.75	-0.11	7.4	59.9	52.5
10	7.52	"	30.05	-0.20	"	21.73	1.06	"	109.95	0.08	"	101.2	93.8
20	7.34	"	29.65	-0.60	"	23.00	2.33	"	109.93	0.06	"	152.1	144.8

**Table 5.** Variations in the chemical composition of the solutions simulating the interstitial waters of the sediments in high-productive regions of the ocean under their interaction with the terrigenous sedimentary matter

of the rocks of low content of bivalent iron, including the suspended and tractional sediments of the continental runoff, amounts to a few mm per 1000 years, or  $n \mu m/year$ . The calculations for x = 0.5 and 1  $\mu m$  show that only small amounts of the solid phase take part in the reaction (8.5 and 14.5%, respectively), even with the overrated x values as such (Table 7). In this case, the above estimate of the supply of dissolved calcium to the ocean resulting from the leaching of terrigenous sedimentary matter (37 million t of Ca per year) should be increased proportionally to the fraction of unreacted matter of the sediment. Hence, the supply of dissolved calcium would amount to 435 and 255 million t/year for x = 0.5 and 1  $\mu m$ , respectively.

**Table 6.** Values of the *a* and *b* parameters in Eq. (6) and those of  $[Si]_{eq}$  and *K* calculated from these parameters

Solution	а	b	[Si] <sub>eq</sub> , µM	K
PW-1	0.0070	0.0600	143	0.12
PW-2	0.0078	0.0493	128	0.16
PW-3	0.0065	0.0554	154	0.12
PW-4	0.0069	0.0473	145	0.15
Average			$142 \pm 11$	$0.14\pm0.02$

These values are comparable to the total runoff of dissolved calcium (650 million t/year) and exceed by 3- to 5-fold the amount of calcium transformed into the soluble state under the erosion of silicate rocks (83 million t/year [7]) and capable of binding  $CO_2$  formed in the ocean under the oxidation of organic matter.<sup>2</sup>

Despite the roughness of the given estimates, the results of the performed experiments point conclusively to the significant role of the continental runoff of solid matter in the geochemical balance of dissolved calcium in the ocean. Later on, the authors intend to carry out analogous experiments on the monomineral fractions of the basic calcium-containing rock-forming silicates. This would allow one to obtain data on the stoichiometry of the reactions of the corresponding minerals with seawater and interstitial solutions of oceanic sediments.

<sup>&</sup>lt;sup>2</sup> The bulk of the Ca<sup>2+</sup> in the continental runoff is a product of the dissolution of carbonate rocks. However, this calcium cannot take part in the immobilization of  $CO_2$  because of the simultaneous supply of equivalent amounts of dissolved bicarbonates forming CaCO<sub>3</sub> in the ocean. The autochthonous CO<sub>2</sub> may be bound exclusively by the calcium not related genetically to carbonate rocks.



**Fig. 2.** Variations of the silicon concentrations in modeling interstitial solution with the increase of the mass (m) of the sample of freshwater ooze. The solutions are as follows: (1) PW-1, (2) PW-2, (3) PW-3, and (4) PW-4.

#### **CONCLUSIONS**

(1) Under the interaction of terrigenous matter (freshwater ooze) with the solutions modeling the interstitial waters of the sediments of high-productive regions of the ocean, the leaching of calcium and silicon proceeds at indifferent behavior of magnesium. During the three-week experiments, 2.3 mg of calcium per 1 g of ooze was transferred to the solution, i.e., only the very surface layers of the grains of the solid phase were involved into the reaction.

(2) In view of the true rate of halmyrolysis of the rocks containing little bivalent iron, which is charac-

<b>Table 7.</b> Calculation of the integrated volume of a halmy-
rolyzed sample of ooze at different depths of a moving front
of the reaction (x)

Grain size, μm	Integrated volume of the reacted sediment, %			
	$x = 0.5 \ \mu m$	$x = 1 \ \mu m$		
≤0.5	0.30	0.30		
≤1	1.22	1.26		
≤5	4.46	6.66		
≤10	5.71	9.01		
≤50	7.87	13.25		
≤100	8.37	14.23		
≤250	8.47	14.44		
≤500	8.48	14.46		
≤600	8.48	14.46		
≤700	8.48	14.46		
≤800	8.48	14.46		
≤900	8.48	14.46		
≤1000	8.48	14.46		

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teristic for the suspended and tractional sediments, the amount of dissolved calcium supplied to the ocean resulting from the transformation of sedimentary matter at the stage of diagenesis amounts to 250-440 million t/year and over. These values are 3- to 5-fold as high as the content of calcium in the continental runoff of dissolved matter supplied by the erosion of silicates. This calcium, unlike that produced by the dissolution of carbonate rocks, is capable of forming carbonate sediments in the ocean under the interaction of autochthonous CO<sub>2</sub>.

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